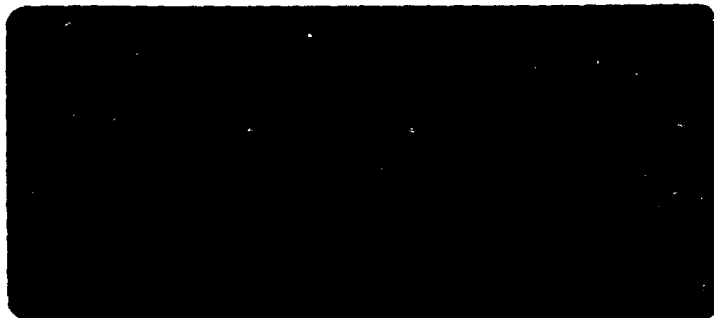
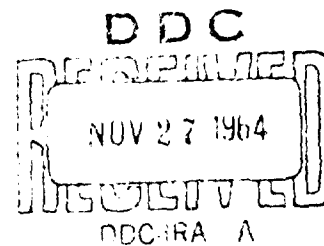


AD 608486



COPY	2	OF	3	mm
HARD COPY	\$.30			
MICROFICHE	\$.50			

Slaps



ARCHIVE COPY

2004 0702047 Best Available Copy

FABRICATION OF BERYLLIUM OXIDE
RADOMES BY PYROLYTIC DEPOSITION

Final Engineering Report
Contract N0w 63-0412-c
National Beryllia Corporation
Haskell, New Jersey

50040705047

FABRICATION OF BERYLLIUM OXIDE
RADOMES BY PYROLYTIC DEPOSITION

Contract N0w 63-0412-c
Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.

Final Engineering Report
for the Period 8 February 1963 to 30 June 1964

Release to ASTIA without restriction. The Contractor imposes no limitation or restriction upon the distribution of this document by the Government to both Government and non-Government recipients.

National Beryllia Corporation
Haskell, New Jersey

ABSTRACT

Research and development work has been conducted with the objective of producing refractory oxide coatings by pyrolytic deposition processes. Beryllium oxide, because of its outstanding physical properties, such as high melting point, high thermal conductivity, low density and electrical characteristics is a strong contender for advanced structural applications. The program was therefore directed toward the preparation of the pyrolytic form of this compound.

A hydro-pyrolytic reaction involving thermal decomposition of beryllium compounds produced in the vapor phase from volatile beryllium halides and oxygen donors such as water vapor was selected for detailed study. The parameters of the dependent and independent variables were partially established and consequently pyrolytic coatings of limited thickness only were produced. The investigation therefore not only demonstrated that pyrolytic beryllium oxide can be prepared but also that continued research is necessary in order to define the controls which must be observed in order to produce the compound in massive form.

Prepared by: George Ferment
George Ferment

Approved by: Philip S. Hessinger
Philip S. Hessinger

W. A. Taebel
Dr. W. A. Taebel

TABLE OF CONTENTS

I.	Introduction
II.	Review of Vapor Plating Processes
III.	Thermodynamics
IV.	Pyrolytic Alumina
4.1	Apparatus
4.2	Vapor Plating Studies
V.	Pyrolytic Beryllia
5.1	Apparatus
5.2	Heating Requirements
5.3	Chlorination of Beryllium
5.4	Vapor Plating Studies
VI.	Beryllia Foams
VII.	Discussion of Results
VIII.	Conclusions and Recommendations
IX.	References
X.	Appendix

LIST OF FIGURES

1. Std. Free Energy of Reaction, Alumina
2. Std. Free Energy of Reaction, Beryllia
3. Water Gas Reaction
4. Alumina Deposition Rig
5. Alumina Deposit
6. BeO Deposition Rig
7. BeO Experimental System
8. BeO Reactor
9. Radome 3-Step Heater
10. Radome Heater Support
11. Std. Free Energy of Be Chlorination Reaction
12. BeO Deposit, 900-1000°C
13. BeO Deposit, 1000-1100°C
14. BeO Deposit, 1100-1200°C
15. Cylindrical Substrate
16. Erosion Effect
17. Crucible Deposit
18. Mounted Crucible Deposit
19. Foam BeO

LIST OF TABLES

- Table I. Process Variables for Alumina Plating
- " II. Range of Process Variables for Beryllia Plating
- " III. Properties of High Purity BeO Foam

FABRICATION OF BERYLLIUM OXIDE RADOMES BY PYROLYTIC DEPOSITION

I. INTRODUCTION

1.1 Purpose of the Program

This program had been oriented to accomplish the following objectives:

- (a) to design and construct experimental equipment for applying refractory oxide coatings by vapor plating techniques
- (b) to conduct a study of radome fabrication utilizing pyrolytic beryllia as the basic material
- (c) to fabricate and furnish sample pyrolytic beryllia radome shapes
- (d) to fabricate and furnish sample composites consisting of pyrolytic coated foam beryllia spheres.

1.2 Present Status

This report will summarize all of the work completed on the pyrolytic deposition program N0w 63-0412-c ending June 30, 1964. During the work period for this contract, Phase (a) described above has been effectively completed. Extensive experiments have been performed to complete Phase (b) and the mechanism of BeO vapor plating was found to be so complex that precise definition of the dependent and

independent variables could not be established and consequently the preparation of massive deposits required for radome fabrication has not to date been achieved. In this investigation the vapor plating of beryllia has been demonstrated to be entirely feasible. However, additional experimentation must be performed in order to establish the engineering parameters involved in producing continuous reproducible deposits.

In this short period of study, only the major obstacles have been identified and before the full utility of this important process can be completely realized, more basic research is necessary to establish the interdependence of all the major variables. Until the mechanism of vapor plating is completely understood, it will be virtually impossible for anyone to prepare structures which comply with design specifications of size, shape, or soundness.

II. REVIEW OF VAPOR PLATING PROCESSES

Vapor plating is a process whereby a volatile material is either thermally decomposed or reacted at the surface of a heated substrate to form a coating. The coating is chemically bonded to the base material and any residual gaseous by-products are continuously removed by a stream of carrier gases or by means of a vacuum. Vapor plating may be carried out over a wide spectrum of temperatures and pressures depending upon

the materials to be plated. In our particular case, we were concerned primarily with the deposition of refractory oxides which are usually plated at temperatures above 1000°C and at atmospheric pressure. For practical application of this technique, the plating material must form volatile compounds which can be easily decomposed or reacted at temperatures below the melting points of either the plating or substrate materials. A further stipulation placed on the volatile compounds, is that they should be sufficiently stable to overcome thermal decomposition before reaching the substrate surface.

There are two general plating methods:

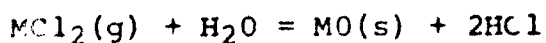
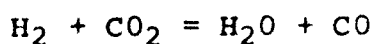
1. reduction or displacement
2. thermal decomposition.

Reduction or displacement plating is in essence a chemical process which involves a reaction between two or more chemical components to form a desired compound. Thermal decomposition depends upon the instability of certain compounds which decompose at critical temperatures to yield a desired coating.

Thus, the deposition of refractory metal oxides may involve the reaction of a volatile oxygen-bearing compound that readily gives up its oxygen. The reactants are transported to a deposition chamber, where under specific conditions they will

react to form the desired oxide with its respective by-product. The reactants may either be premixed or mixed directly at the reaction site depending upon their ability to remain inert in the transfer lines.

Refractory metal halides are generally used in oxide plating because they possess the desirable properties of low vapor pressure at relatively low temperatures and thermal stability at elevated temperatures. Oxygen is conventionally introduced in the form of water vapor which is generated by the reaction between hydrogen and carbon dioxide at the source according to the equation, $H_2 + CO_2 = H_2O + CO$. This reaction is not surface catalyzed and will proceed readily in the forward direction provided the temperature of the gases is greater than 600°C. The water-gas reaction was incorporated primarily to reduce premature hydrolysis of the halides, since they will react rapidly with any water vapor that exists in the vapor space forming finely suspended hydroxides, oxyhalides, or oxides. Thus, it is essential that all components retain their individual identities until they reach the substrate where they spontaneously react in the following steps:

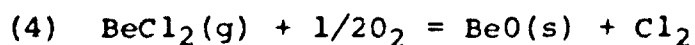
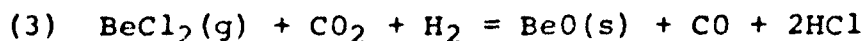
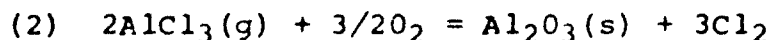
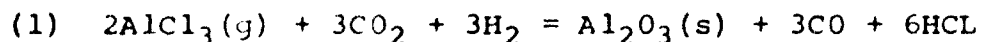


to produce the pyrolytic deposit.

III. THERMODYNAMICS

Vapor plating of refractory metal oxides is a chemical process which occurs at elevated temperatures. Thus, thermodynamic principles may be employed to analyze various reactions and enable us to select those which are thermodynamically feasible.

Four major plating systems were analyzed, two for the vapor plating of alumina and two for the vapor plating of beryllia. The overall reactions for each system are represented by the following four equations:



The standard free energy change for each reaction was calculated and is graphically presented in Figures 1 and 2.

The method of calculation employed the familiar Law of Hess, which states that the summation of the standard free energies of formation of the products minus the reactants is equal to the standard free energy change of the reaction. If the result of this calculation is negative, it means that the reaction will proceed spontaneously and is therefore thermo-

dynamically feasible. It is evident from Figures 1 and 2 that vapor plating of both alumina and beryllia, for the systems considered, is thermodynamically feasible.

Figure 3 shows the relationship between the standard free energy of reaction versus temperature for the water-gas reaction. Here it is evident that the reaction proceeds spontaneously only at temperatures above 1100°K.

It must be remembered that these calculations only represent the overall reaction and only show that the reaction is thermodynamically possible. It does not show us the rate or mechanism by which each system approaches equilibrium for this cannot be predicted by theoretical considerations. In order to establish the reaction kinetics for each vapor plating system recourse to direct experimentation is necessary.

IV. PYROLYTIC ALUMINA

Although the specific purpose of this program was to develop techniques for vapor plating beryllia, initial studies were performed using alumina as the model system in order to establish the factors and problems of hydro-pyrolytic deposition by means of a volatile metal halide without encountering the hazards of beryllia's toxicity.

4.1 Apparatus

The experimental apparatus featured simple design consisting

essentially of two major components:

1. The deposition chamber, and
2. A vaporizer.

The deposition chamber was composed of a Pyrex bell jar which was fitted to a brass base plate and when properly sealed was capable of withstanding both vacuum and pressure. The vaporizer consisted of a Vycor tube which was wrapped with heating tape. The entire experimental system is depicted schematically in Figure 4.

Substrate heating requirements were initially met by a resistance coil that was placed inside a cylindrical ceramic tube 1/2" X 3". Later, a new system was incorporated utilizing a ceramic muffle furnace whereby flat substrates 1 in. sq. could be be heated.

4.2 Vapor Plating Studies

In the initial runs, the cylindrical substrate was used, however, it soon became evident that the plating process, based on aluminum chloride as the limiting reactant, was very inefficient yielding conversions to the oxide formed on the substrate of less than 1 percent. To remedy the situation, a flat substrate was utilized whereby the reactant gases would be forced directly on the substrate, thus providing more intimate contact between substrate and reactants. This resulted

in a plating efficiency of approximately 12 percent. For this series of experiments, the process variables were at those levels listed in Table I.

TABLE I

Process Variables for Alumina Plating

H₂ - 2.0 liters/min.

CO₂ - 0.25 liters/min.

AlCl₃ - 0.5 grams/min.

Substrate temperature - 1000-1100°C.

The major problem encountered with this system was controlling the rate of sublimation of aluminum chloride, thus making it difficult to control the concentration of aluminum chloride in the vapor stream. However, even with this uncontrollable parameter, alumina deposits were obtained in the temperature range 1000 to 1100°C. The coatings were ranged from .5 to 2 mils. A typical deposit is shown in Figure 5. The coated substrates were subjected to x-ray diffraction analysis and the results were conclusive that alpha alumina was definitely deposited. A condensed summary of the runs made with aluminum chloride as the source material is given in the Appendix: Tabulation of Hydro-Pyrolytic Experiments.

V. PYROLYTIC BERYLLIA

5.1 Apparatus

Extension of the hydro-pyrolitic program to vapor plating beryllia necessitated the design of a new experimental system to safely handle the beryllium compounds. Alumina plating was performed in a simplified system. However, the purpose of these investigations was to gain techniques and establish the problems encountered with a halide vapor plating process before proceeding to the toxic beryllia process.

The beryllia system was designed for the ultimate goal of vapor plating beryllia on large radome substrates. Thus, equipment design was guided by radome specifications. The apparatus must be large enough to handle conical radomes possessing a 9 cm base and 15 cm altitude. Also, because of beryllia's hazardous nature, it was necessary to incorporate in the design of the experimental system safety features which would provide adequate ventilation in case of a possible breakdown. To meet these requirements, a hood was designed and fabricated to completely house the vapor plating apparatus.

The hood was an 8' X 8' X 4' structure provided with adequate ventilation to quickly remove any dust or vapors which might leak from the experimental equipment.

The experimental equipment features simple design consisting

of two main components: (1) a chlorinator, which will convert beryllium metal directly to the halide, thus eliminating the sublimation problem encountered in alumina plating and (2) a beryllia plating chamber, which permits the reactants to combine at the substrate.

The chlorinator was a nickel vessel which was charged with beryllium chips. Hydrogen chloride gas was passed through a metal bed where it reacts to form the volatile chloride, which is then transported to the plating chamber. Here the vapor stream mixes with the other reactants and forms the oxide layer on the substrate. The vapor plating chamber was a cylindrical vessel which was provided with circular end plates and O-ring seals to insure a pressure-tight system. The chamber was also equipped with water cooling coils in order to keep the chamber walls at a safe temperature below that which would cause the destruction of the O-ring seals. Cooling the chamber also minimizes the corrosive action of the reacting gases on the chamber walls. The material construction was brass which was electroplated with a layer of nickel for high temperature corrosion resistance. A schematic diagram and photographs of the experimental setup are shown in Figures 6, 7 and 8.

5.2 Heating Requirements

A major requirement of this process is that of supplying enough heat to keep all of the major components of the entire system at the proper operating temperatures.

In order to prevent condensation of the beryllium chloride vapor, it was necessary to maintain all process lines at temperatures above 400°C. This was accomplished by wrapping the lines with heating tape and regulating the power input in order to produce the desired exit temperatures of the process streams.

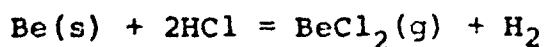
The beryllium chlorinator was also wrapped with heating tape in order to bring the beryllium chips to the proper temperature, between 500 and 600°C, in order to promote the chlorination reaction.

The substrate heating requirements can be met in a number of ways depending upon the substrate geometry. The conical radome heating requirements were met with a three-step alumina heater which was wound with molybdenum resistance wire. The design is shown in Figure 9. Figure 10 shows how the heater is mounted in the plating chamber. This heater was specifically designed to provide uniform heating, however, actual tests showed that there existed a temperature gradient of 100°C from the top to bottom of the radome. This heater design was sufficient for heating radomes to operating temperatures of 1200°C.

For temperature exploration above 1200°C, it was advantageous to modify the system to accommodate smaller substrates such as ceramic cylinders, ceramic crucibles and flat ceramic. The heating requirements for these substrates were met by a 2 in. alumina muffle furnace which could produce a maximum operating temperature of 1600°C.

5.3 Chlorination of Beryllium

The first major step leading to pyrolytic beryllia is the formation of the volatile beryllium chloride. The direct chlorination of beryllium metal was utilized in order to overcome the difficulty that was encountered with the sublimation of aluminum chloride. Thermochemical calculations revealed that the chlorination of beryllium according to the reaction:



was thermodynamically feasible. The free energy of this reaction is plotted in Figure 11.

The chlorination reaction was performed at 500°C and was found to be approximately 75 percent efficient, based on HCl as the limiting reactant for the range of flowrates 0.1 to 1.0 liters/min. Thus the concentration of beryllium chloride in the process flow streams can be strictly controlled by manipulating the hydrogen chloride flowrate.

5.4 Vapor Plating Studies

The basic objective of this program was to develop a process whereby dense pyrolytic BeO coatings could be vapor plated on beryllia radome substrates. Naturally, the first phase of such a program would be to decide upon a reaction which is thermodynamically feasible and will yield the desired products. Thermochemical calculations for two vapor plating reactions were presented in an earlier section. The results showed that the hydrolysis of beryllium chloride via the water gas reaction was most favorable and therefore was the reaction considered in this study. Naturally, such a study embraces a wide spectrum of variables and therefore, it was necessary to select a range of variables which, if they did not capture the optimum set of conditions, they at least would indicate a definite path to follow in order that an optimum be approached. The range of experimental variables encountered in this study are given in Table II, and a condensed summary of the runs made with beryllium chloride as the source material is given in the Appendix: Tabulation of Hydro-Pyrolytic Experiments.

TABLE II

Range of Process Variables for Beryllia Plating

Temperature range	- 900 to 1500°C
HCl flowrate	- 0.1 to 1.0 liters/min.
CO ₂ flowrate	- 0.1 to 3.0 liters/min.

H₂ flowrate - 3.0 liters/min.

H₂O:BeCl₂ - 1:1 to 15:1

All coatings obtained in this study were evaluated by both gain in substrate weight and by metallographic examination.

Initial experiments used beryllia radomes measuring approximately 4 in. across the base and 6 in. high as substrates and were designed to study the effect of temperature on the plating process. All other parameters were fixed at the following levels:

HCl 1.0 l/min.

CO₂ 3.0 l/min.

H₂ 3.0 l/min.

Using such large substrates, of course, imposed limitations in that it restricted the substrate temperature attainable in the initial rig to a maximum level of 1200°C. This consequently reduced our experiments to the temperature ranges 900, 1000, 1100 and 1200°C. For each temperature range, several experimental runs were made, plating successive deposits on the same radome. Each run lasted approximately 60 minutes, during which time 1 to 2 grams of pyrolytic beryllia was deposited corresponding to a deposition rate of approximately 1 mil/hr. When the radome showed a total weight gain anywhere from 3 to 5 grams, it was sectioned, mounted, and examined metallographically to determine the fine structure of the deposit.

Pyrolytic coatings were obtained in all three temperature ranges, as identified by methods previously described. However, the significant fact is that in each range the pyrolytic coating possessed a slightly different crystalline structure.

In the low temperature range, 900 to 1000°C, the coating was characterized by large amounts of whiskers growing radially outward from the surface. The whiskers were plainly visible without magnification and were later identified as monocrystalline BeO growing along the C-axis. A typical coating is shown in Figure 12. The thickness of the coating varied from 15 to 150 microns, (.0006 - .006") with an average thickness of 40 microns.

As the deposition temperature was increased to the range of 1000 to 1100°C, the quantity of whiskers growing on the radome was reduced to approximately 10% of that obtained at the lower temperatures. The pyrolytic coating was also different, looking somewhat like compacted snowflakes with fibers growing in random directions. Again, the coating was not uniform but varied in thickness up to 150 microns, possessing an average of 50 microns. Figure 13 shows a typical deposit.

When the deposition temperature was increased to the higher range, 1100 - 1200°C, all whisker-like deposits disappeared. The coating looked as if it were being progressively compacted and densified in a layer adjacent to the substrate.

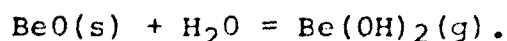
This coating is shown in Figure 14, which possesses an average thickness of 40 microns.

For all temperature ranges, the pyrolytic coating was non-uniform and porous, however, the experiments did indicate that a higher deposition temperature was necessary if dense pyrolytic coatings are to be obtained.

Before the higher temperature series of experiments could be performed, some modifications were necessary in the experimental equipment. The heater was now designed to accommodate a cylindrical substrate (1" X 6") to facilitate obtaining higher operating temperatures. Also, in the first series of experiments, it was noted that a large excess of active beryllium chloride remained in the vapor plating chamber, indicating an incomplete reaction with the available water vapor. Thus, for the next series of experiments the hydrogen chloride flowrate was reduced to the order of 0.4 liters/min. which essentially increases the $H_2O:BeCl_2$ ratio from that previously used.

The initial temperature runs of 900 to 1200°C were studied in order to determine if this new cylindrical system was similar to the radome substrate system. The deposits produced in this temperature range were quite similar to those obtained in the radome experiments. A typical substrate, as it was removed from the plating chamber, is shown in Figure 15. Runs were

also made at 1300, 1400 and 1500°C, however, no appreciable deposits were detected by either weight gain or by metallographic examination of the substrate after it had been brushed with a stiff bristle brush under running water. However, metallographic examination of the substrate specimens revealed that the deposit appeared as if it had been subjected to erosion during the pyrolytic process. A sample showing this effect is given in Figure 16. Erosion could have occurred because there existed a large excess of water vapor, and at high temperatures the reversible hydrolysis of beryllium oxide can occur,



The high excess of water vapor was eliminated by reducing the flowrate of carbon dioxide to rates of the order of 0.1 l/min. Carbon dioxide was therefore the limiting reactant in the water-gas reaction. The high temperature experiments were repeated again using the following flow levels:

HCl	0.4 l/min.
CO ₂	0.1 l/min.
H ₂	3.0 l/min.

Again significant deposit was detected after washing the substrate. A possible explanation for this result is that at the higher temperatures the water-gas reaction is accelerated in the vapor space at some distance from the substrate and the water vapor which is formed reacts prematurely with the

beryllium chloride producing either hydroxides, oxychlorides, or oxides of beryllium. Such premature formation prevents orderly deposition from occurring and consequently only a loosely compacted easily removable coating is obtained.

The next series of experiments was designed to minimize the degree of premixing by forcing one gas stream to flow parallel to the other gas stream as they flowed along the side of a cylindrical substrate. This was to be accomplished by introducing the CO_2 stream up through the cylindrical substrate and then deflecting the stream by means of a beryllia crucible inverted over the cylinder so that the stream would flow down along the sides of the cylindrical substrate. However, after a few preliminary runs were made, it was constantly observed that the deposition did not occur along the lateral area of the cylinder extending below the capping crucible but that a deposit actually occurred on the outer wall of the beryllia crucible. It appears that the descending gases, in this case hydrogen and beryllium chloride, create a turbulence along the sides of the crucible. This turbulent action causes some carbon dioxide, which was not completely deflected downward to mix with the downward flowing gas stream. Thus, all gas streams combine directly at the crucible resulting in a pyrolytic deposit. These deposits have been quite large, in some

cases weight gains of more than 1 gram have been recorded for a single run. However, all deposits tended to be gritty, porous, and in general, lacking in good quality. A typical pyrolytic deposit as obtained on a crucible is shown in Figure 17; while Figure 18 is a mounted section showing the fine structure of the deposit. Thus it is evident that intimate mixing of the reactants at the substrate is necessary if large deposits are to be obtained.

The next series of experiments was designed to improve the quality of the deposit. Reducing the hydrogen chloride flow-rate should in turn reduce the rate of pyrolytic deposition. Slower deposition rates should improve the quality of the crystalline deposit and produce a dense coating. Hydrogen chloride was varied from 0.4 to 0.1 l/min, while the other variables were fixed at the at the following levels:

Temperature	1300°C
CO ₂	0.16 l/min.
H ₂	3.0 l/min.

Metallographic examination of the pyrolytic samples did not show any improvement in the quality of the deposit over those previously obtained. It appears that the turbulent action which mixes the two flow streams also produces by its action

a coarse, porous deposit.

In the final series of experiments, an attempt was made to place a coating on a flat 1" X 1" substrate. Both gas streams entered the plating chamber through ceramic tubes located approximately 1" above the substrate and impinged at various angles directly on it. Other experimental conditions were the same as in the previous series and again the results were considered negative.

In these experiments, plating times varied from 1/2 to 8 hours with the majority of the runs lasting 1 hour. However, there was no significant trend as to how plating time affected either the magnitude or quality of the deposit.

IV. BERYLLIA FOAMS

A prototype beryllium oxide foamed ceramic sphere, three inches in diameter, and a typical cylindrical blank from which the sphere was produced are shown in Figure 19. Selected physical and electrical property data on this high purity (99.9% BeO) oxide foam are listed in Table III.

Several interesting observations are apparent in comparing the properties of pure BeO foams to the 98% BeO foams previously reported. As expected the dissipation factor at comparable

temperature and frequency test conditions is appreciably lower for the purer material.

Foams of significantly lower density, under similar fabrication conditions, may be produced from the pure BeO ceramic powders using the all-organic setting systems. Minor variations in process conditions make possible a wide range of product densities allowing structure properties such as dielectric constant, strength and average pore size to be "tailored" to meet particular design requirements.

The dielectric constant appears to be more dependent upon foam density than on minor changes in composition. Measurement of this parameter is complicated by an apparent change in value when the 2" diameter by 3/4" disc sample is simply turned over and remeasured. It is believed that this difference results from the sample preparation procedure and test apparatus which necessitate thin aluminum foil electrodes being affixed to each face of the disc. It is likely that the actual surface contact area of aluminum foil to dense ceramic webbing in a structure 85% air is different at the two disc faces and that this difference is responsible for the apparent change in dielectric constant. Since the application frequency is much higher than those used in these preliminary screening,

TABLE III

Properties of High Purity BeO Foam

Density: 0.43 g/cc 14.3% of theoretical

Porosity: 85.5% by weight water absorption

Avg. Pore Size: 500 microns

Composition: 99.9% BeO

<u>Dielectric Constant (25°C)</u>		<u>Frequency</u>
Side 1 up	2.932	500 kc

Side 2 up	2.410	500 kc
-----------	-------	--------

Side 1 up	1.694	1 mc
-----------	-------	------

Side 2 up	2.150	1 mc
-----------	-------	------

<u>Dissipation Factor (25°C)</u>		<u>Frequency</u>
Side 1	0.0055	500 kc

Side 2	0.0067	500 kc
--------	--------	--------

Side 1	0.0021	1 mc
--------	--------	------

Side 2	0.0023	1 mc
--------	--------	------

up in the range where the test methods and fixturization will be significantly different from those presently employed, the noted variation will probably not be troublesome. For screening purposes geometric considerations suggest the higher of two differing values is the most meaningful.

VII. DISCUSSION OF RESULTS

The results of this study are in no way conclusive and even a qualitative interpretation is extremely difficult. It was obvious from the initial series of experiments that temperature has an important role in establishing the quality of the coating. An increase in temperature definitely reduces porosity and densifies the coating, although this statement could not be verified above 1200°C using the hydro-pyrolytic process. However, it is believed that the poor deposits obtained above 1200°C are largely due to premature reactions occurring in the vapor space, leaving little or no reactants to combine at the substrate.

Also, if smooth, continuous coatings are to be obtained from the hydro-pyrolytic process, it seems evident that they will have to be deposited from parallel but opposite flowing gas streams moving in laminar flow. Under ideal conditions there should be no mixing and all mass transfer would occur

by the mechanism of diffusion. Although this is an ideal case it will certainly have to be approached in order to minimize non-uniformity and spurious crystal growth.

VIII. CONCLUSIONS AND RECOMMENDATIONS

Analyses of the results obtained during the foregoing experimental program have led to the following conclusions:

- (1) Pyrolytic deposition of beryllium oxide is feasible from the standpoint of thermodynamics and the chemistry of various selected reactants.
- (2) The majority of the effort has been centered about utilization of the beryllium chloride pyrolysis and it has been found that the reactions involved are exceedingly complex and the number of variables present are such that practical limitations exist in the use of this system for pyrolytic deposition.
- (3) In spite of the difficulty involved in controlling the deposition of beryllium oxide, reasonably dense pure deposits have been built up to thicknesses of approximately .005". Attempts to build thicknesses up to the desired objective of .050" generally resulted in accumulation of sporadic and fibrous type surfaces.

(4) It has been found in general that physical characteristics of the deposited coating are temperature-dependent with most promising characteristics being developed at temperatures above 1200°C.

(5) Preparation of beryllium oxide foamed spheres having the desired dielectric and density properties has been shown feasible, although because of limitations in the control of pyrolytic process, coating of such spheres by this technique has not been achieved within the present effort.

Based on the above conclusions, we feel it in order to make the following recommendations with regard to future activities in this area.

The thermochemical reactions involved in the vapor deposition of pure refractory oxide systems, particularly in cases where relatively thick sections are required and for comparatively large surface areas become extremely complex and difficult to control unless a thorough knowledge of processing parameters is established. We suggest, therefore, that more emphasis be placed in the immediate future on a research oriented study aimed not at preparation of useable hardware but at developing a better understanding of the physical and chemical principles involved in pyrolytic deposition of

refractory oxides. This process should be studied in a program embodying the concepts of statistical design of experiments in order to minimize the tedious and repetitious processes required and to achieve maximum results in the shortest possible time. We feel that the results which were obtained to indicate that such techniques can be developed and applied to the preparation of useable end items included not only radomes but ultimately, various sizes and shapes of microwave windows, re-entry structures, protective coatings and electronic devices such as capacitors, insulators and substrates.

IX. REFERENCES

1. Powell, C. F. and Campbell, I. E., "The Formation of Metallic Coatings by Vapor-Phase Techniques", METAL FINISHING, April 1952, pp. 64 - 69.
2. Browning, M. F. et al, "Alumina Coating of UO_2 Shot by Hydrolysis of Aluminum Chloride Vapor", Report No. BMI-1471, Contract No. W-7405 eng-92, Battelle Memorial Institute, October 25, 1962.
3. Van Houten, G. R. White, J. F., and Botje, J. M., "Formation of Alumina Coatings on Beryllia by a Vapor Deposition Process", APEX-699, Contract Nos. AF 33(600)-38062 and AT (11-1)-171, General Electric Co., N.M.P.O., June 30, 1961.
4. Krier, C. A., "Coatings for the Protection of Refractory Metals from Oxidation", DMIC Report 162, Defense Metals Information Center, Battelle Memorial Institute, November 24, 1961.
5. Blicher, J. N., Jr., and Oxley, J. H., "Chemical Vapor Deposition Opens New Horizons in Ceramic Technology", BUL. AM. CERAM. SOC. 41(2)1962(81-85).
6. Blocker, J. M., Jr. et al, "Chemical Vapor Deposition", DMIC Report 170, Defense Metals Information Center, Battelle Memorial Institute, June 4, 1962.

STANDARD FREE ENERGY OF REACTION

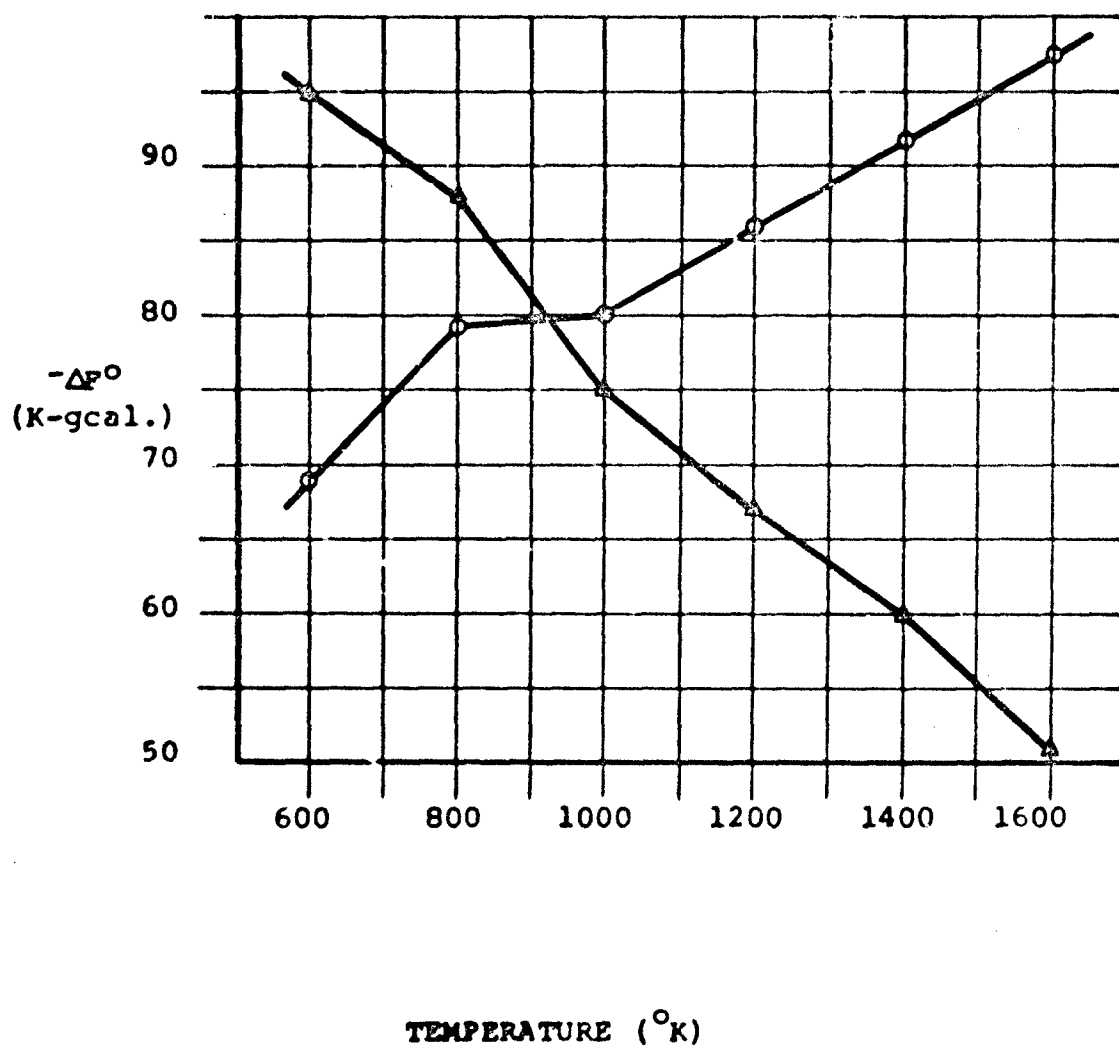
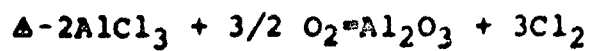
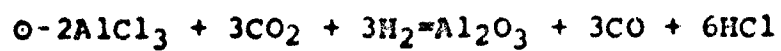


FIGURE 1

STANDARD FREE ENERGY OF REACTION

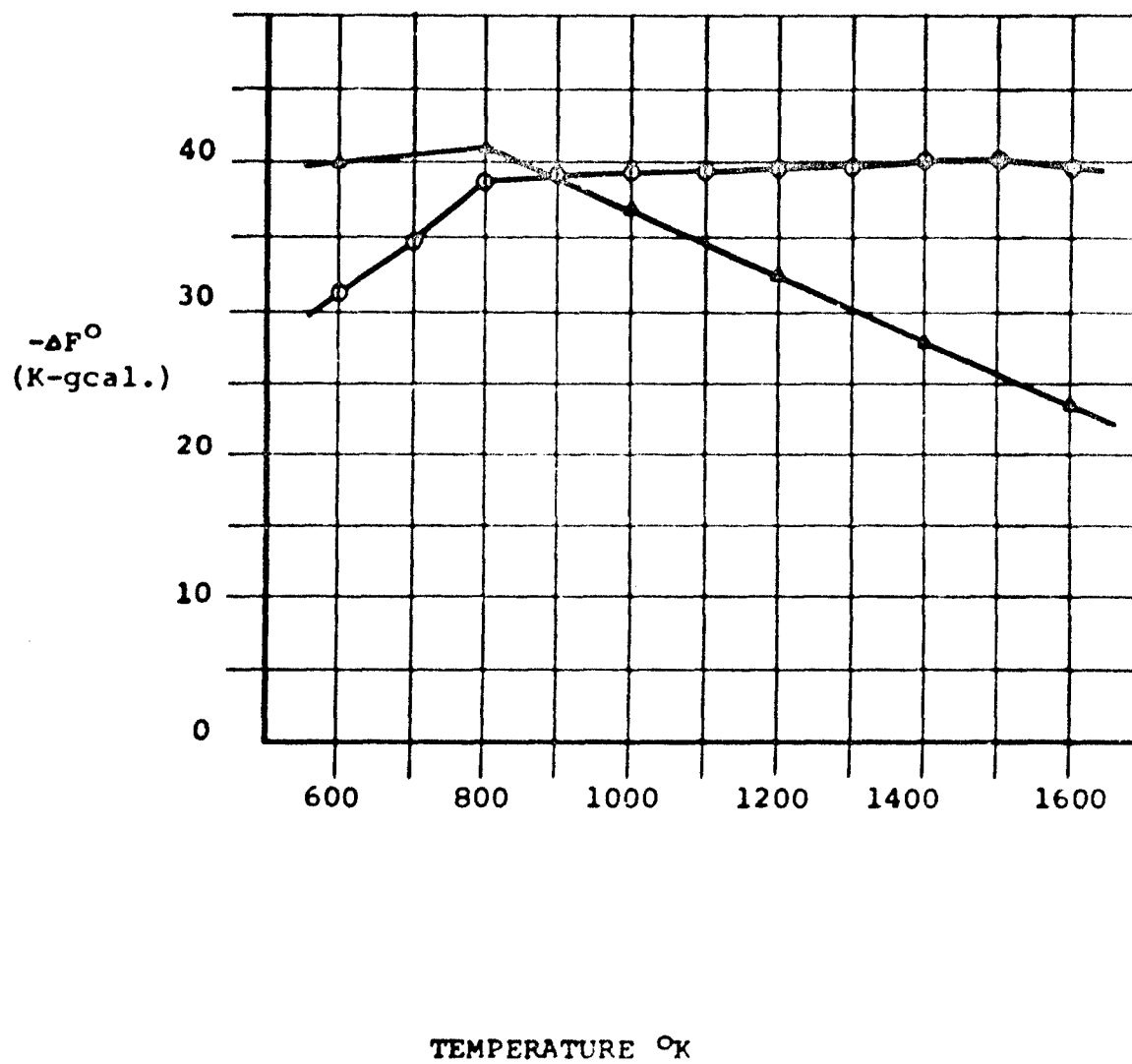
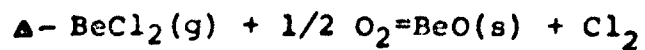
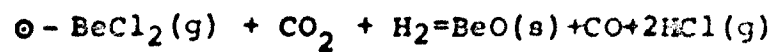


FIGURE 2

STANDARD FREE ENERGY OF REACTION

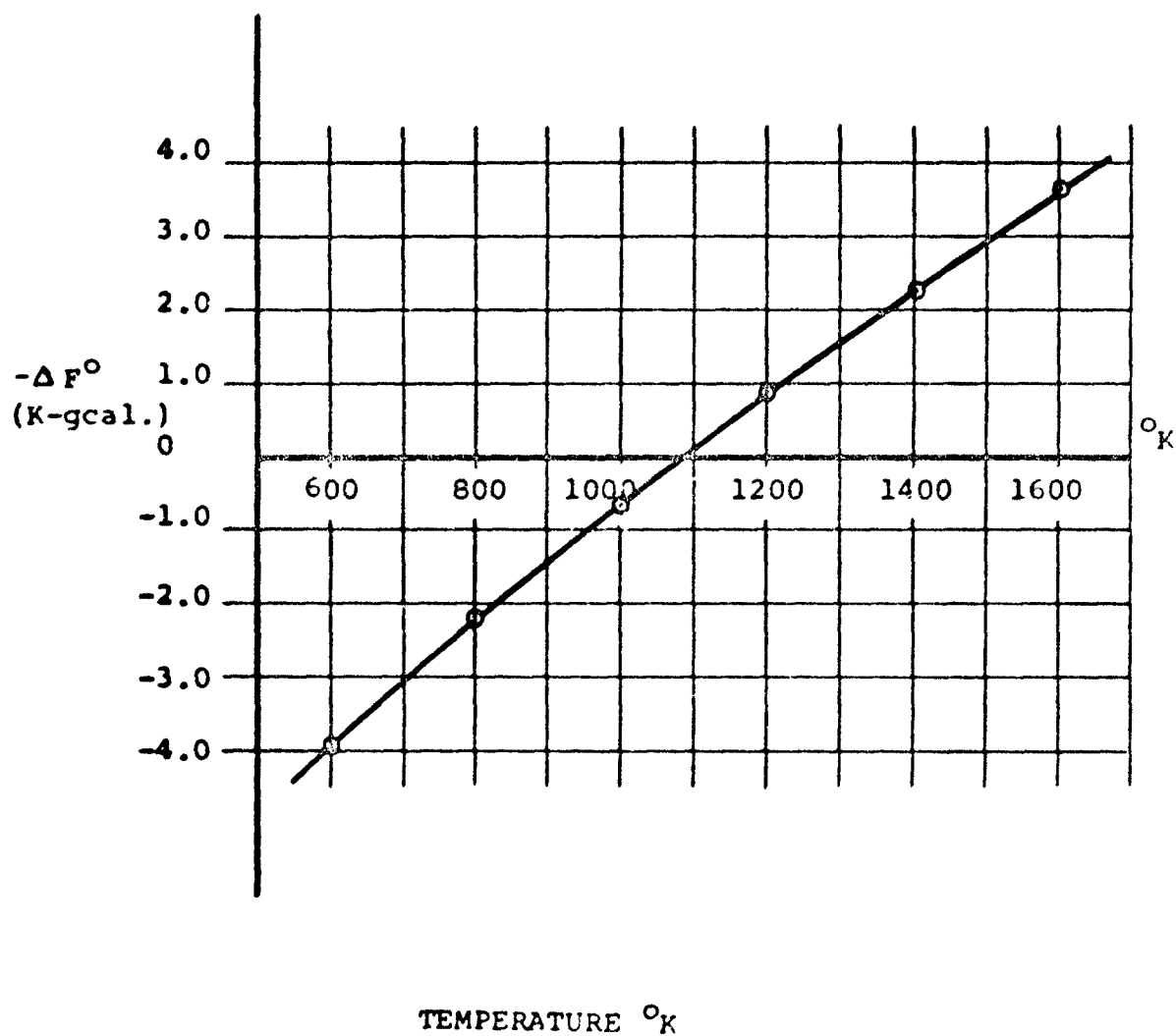
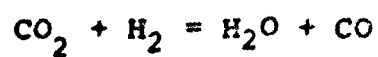


FIGURE 3

SCHEMATIC OF DEPOSITION SYSTEM

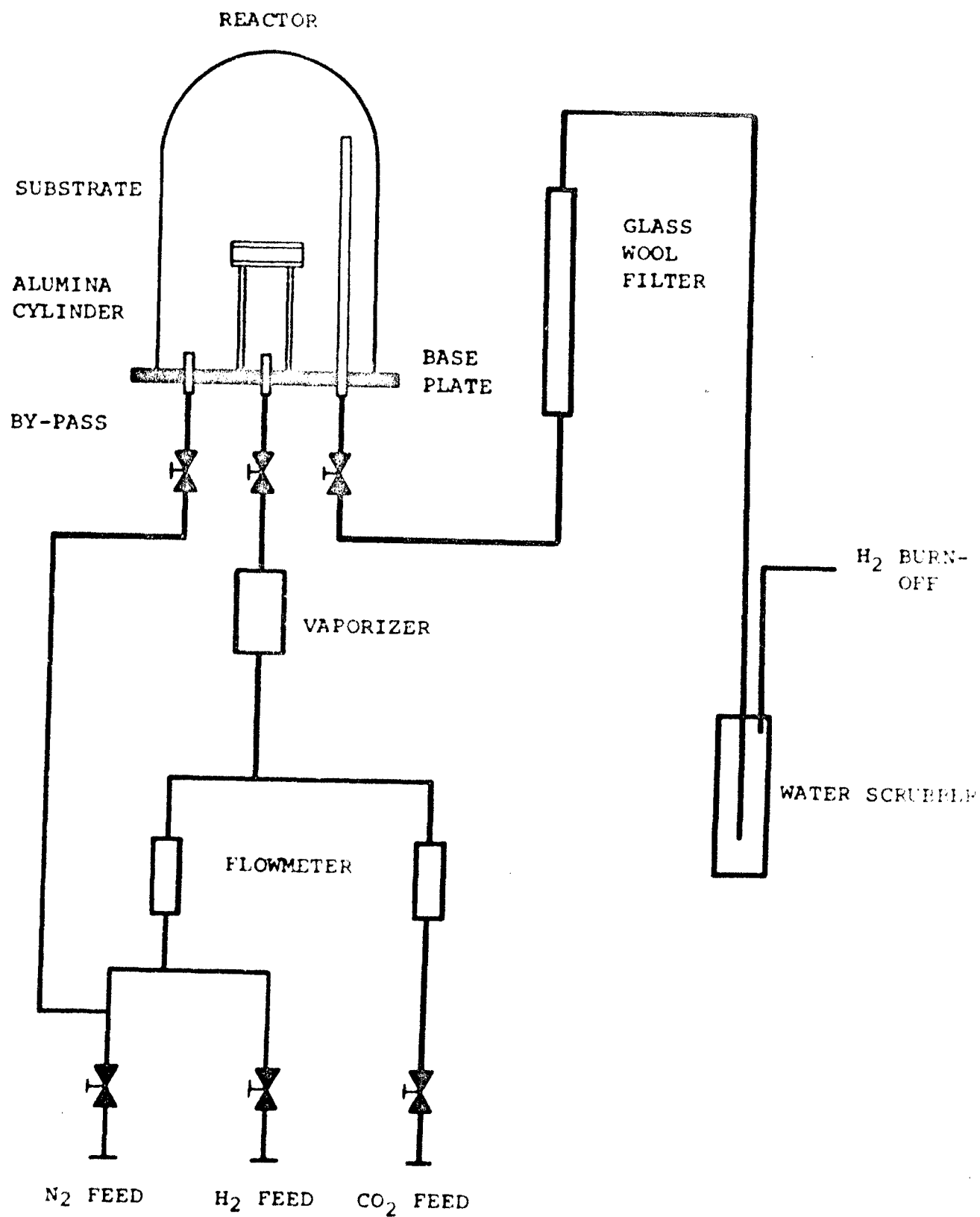


FIGURE 4

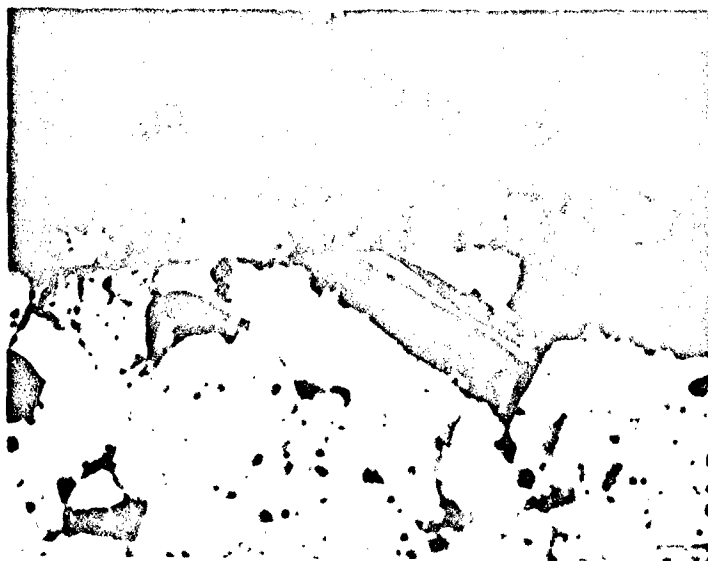


Figure 5

PYROLYTIC ALUMINA
DEPOSITION TEMPERATURE 1000-1100°C
MAGNIFICATION 130X

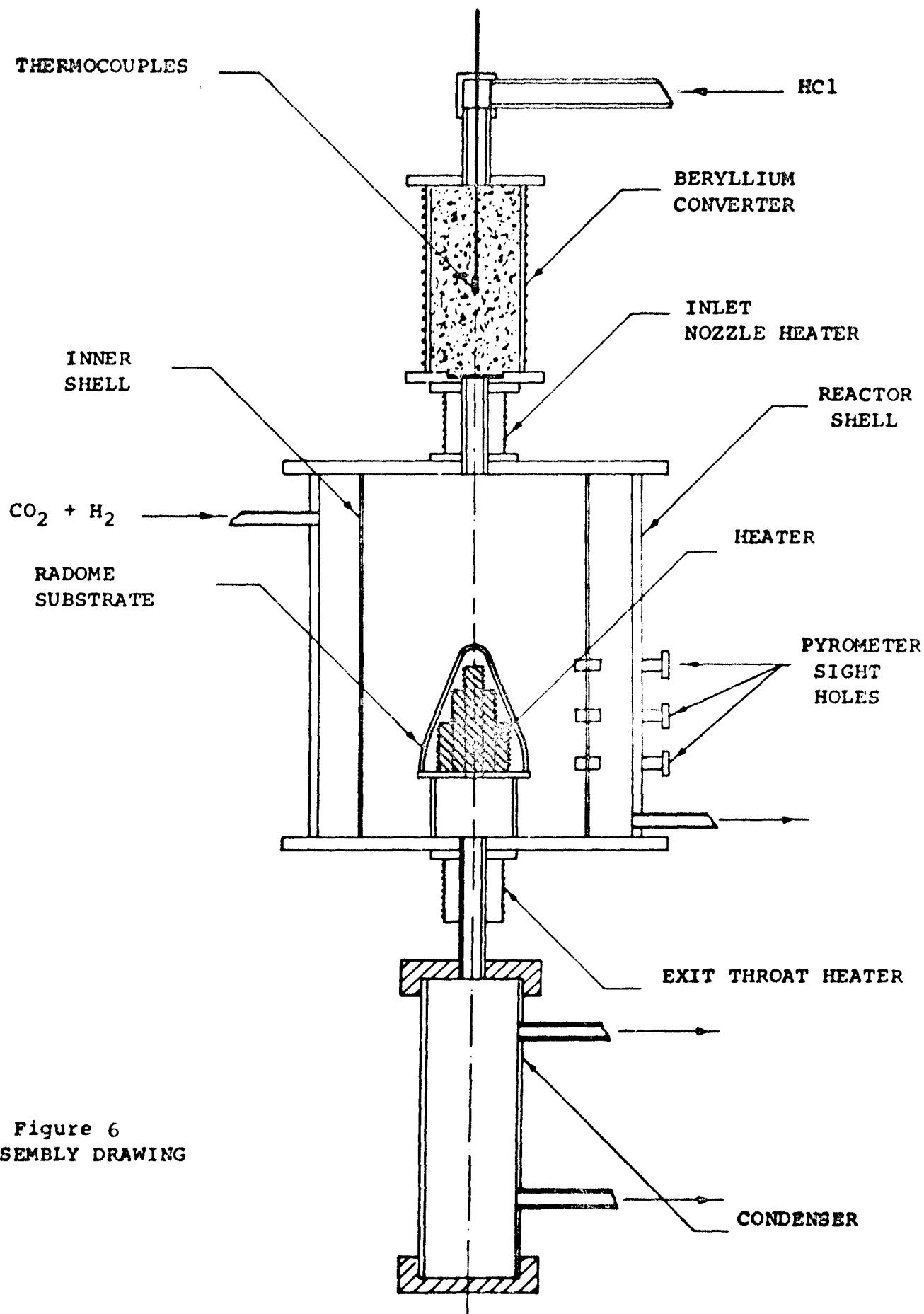


Figure 6
ASSEMBLY DRAWING

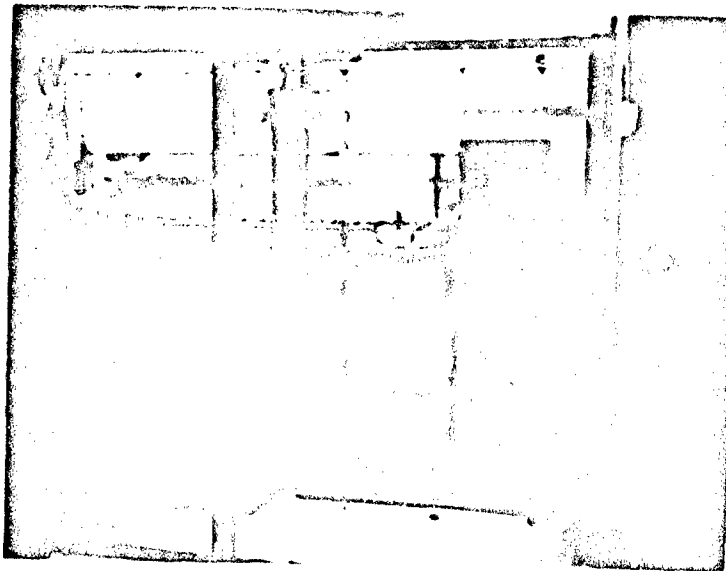


Figure 7

EXPERIMENTAL SYSTEM

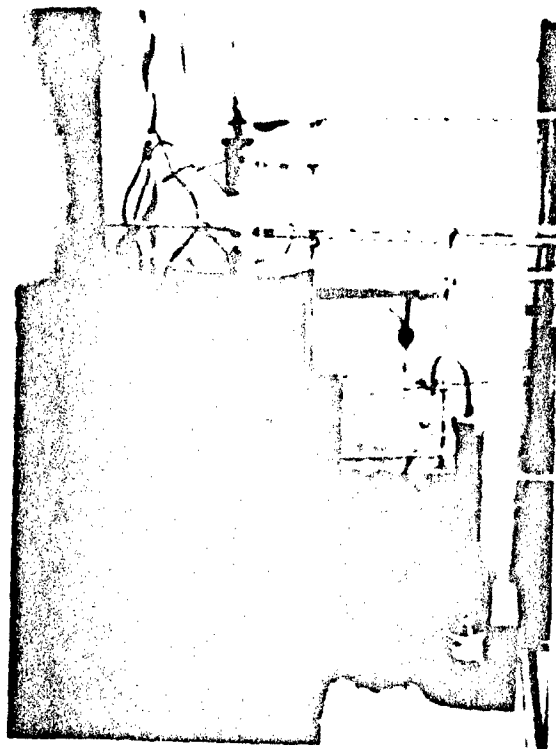


Figure 8
DEPOSITION CHAMBER

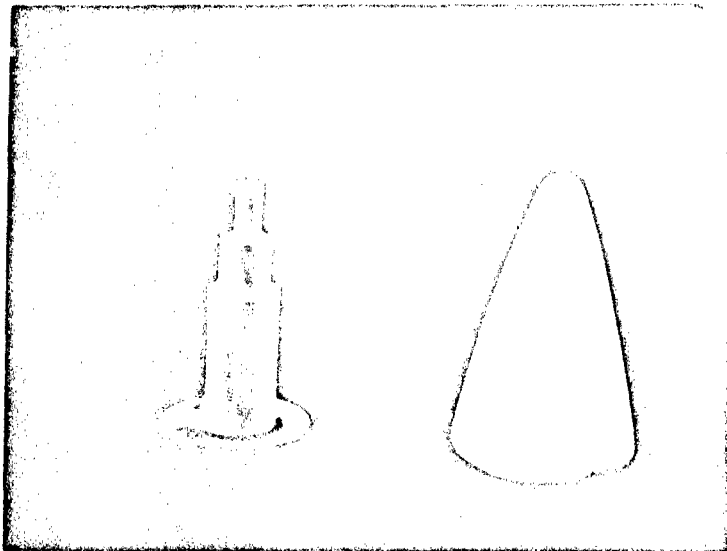


Figure 9

ALUMINA HEATER

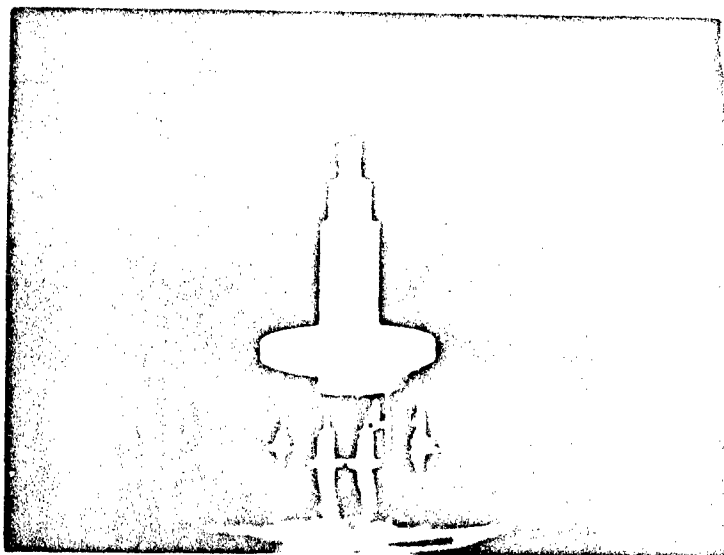


Figure 10

HEATER AND RADOME SUPPORT STAND

STANDARD FREE ENERGY OF REACTION

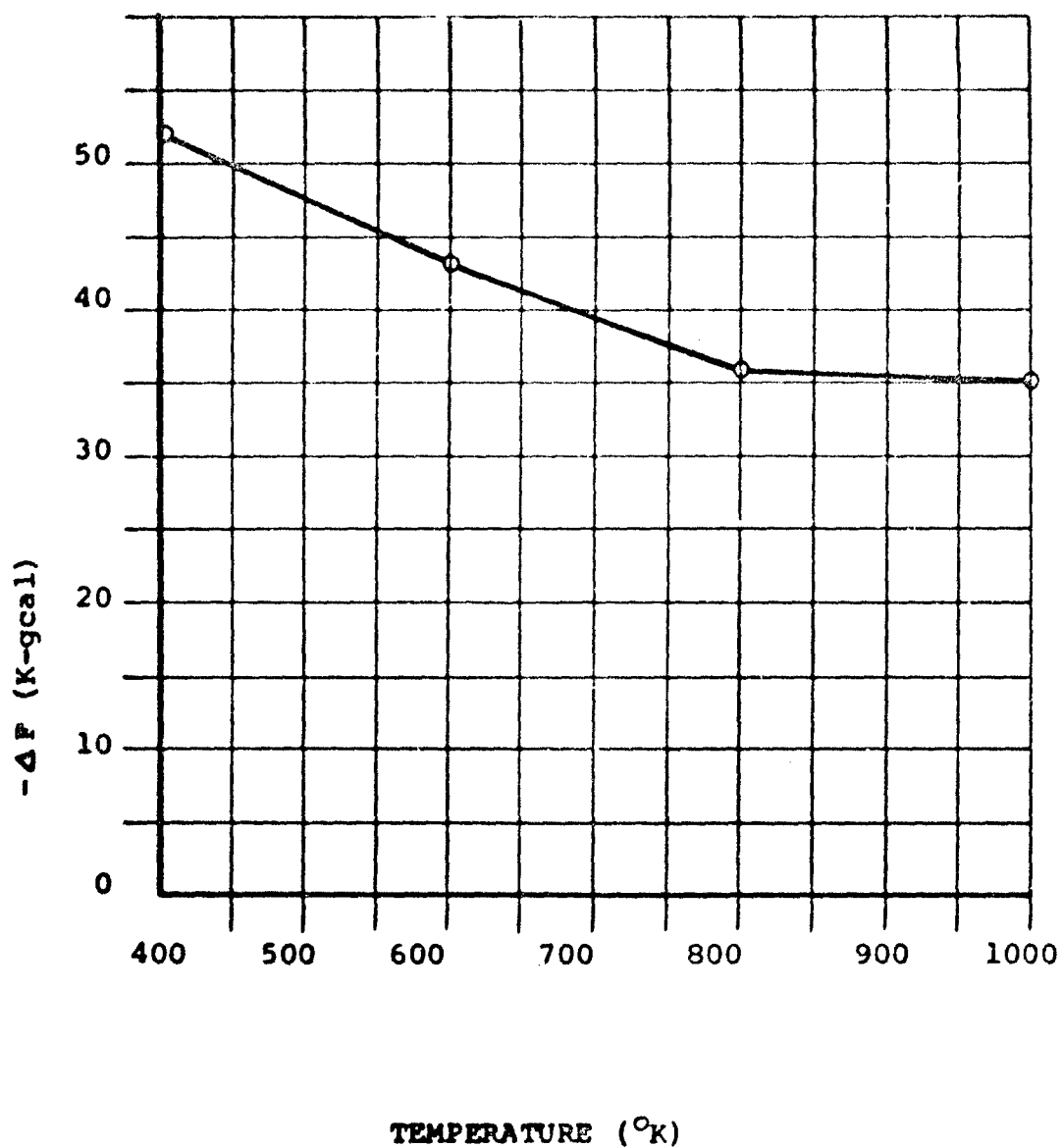
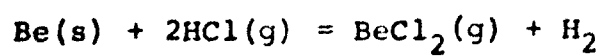


FIGURE 11

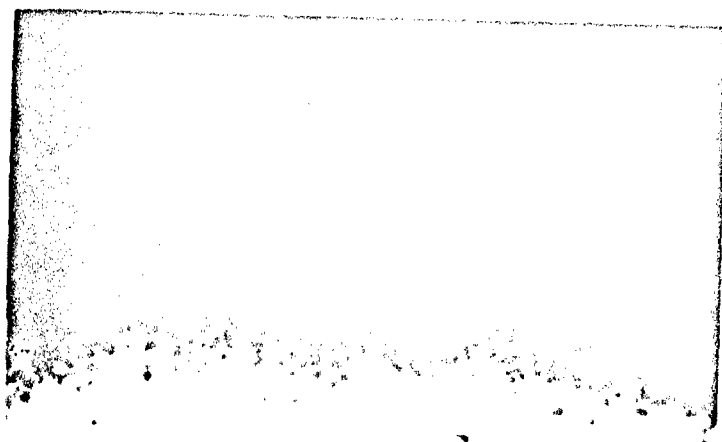


Figure 12

PYROLYTIC BeO
DEPOSITION TEMPERATURE 900-1000°C
MAGNIFICATION 130X

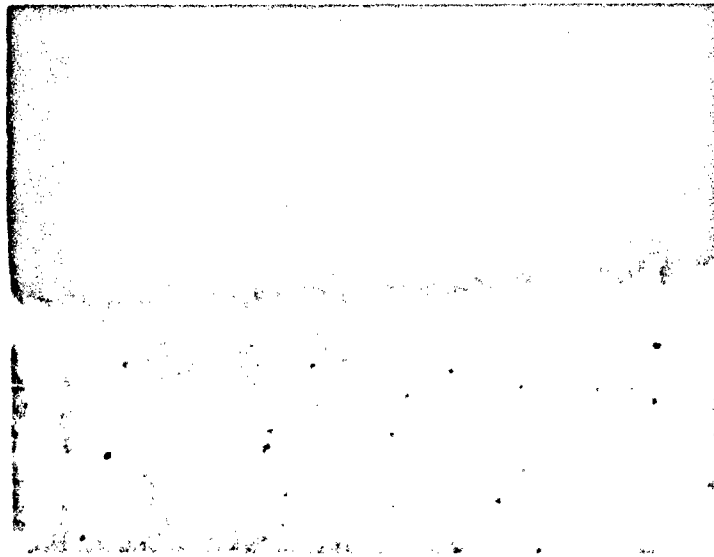


Figure 13

PYROLYTIC BeO
DEPOSITION TEMPERATURE 1000-1100°C
MAGNIFICATION 130X

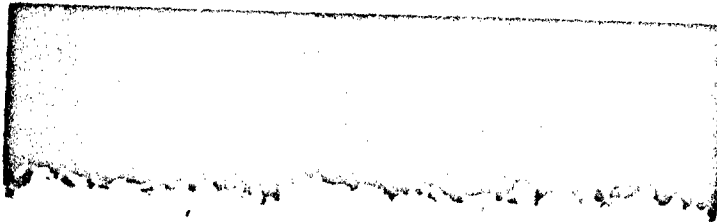


Figure 14
PYROLYTIC BeO
DEPOSITION TEMPERATURE 1100-1200°C
MAGNIFICATION 130X

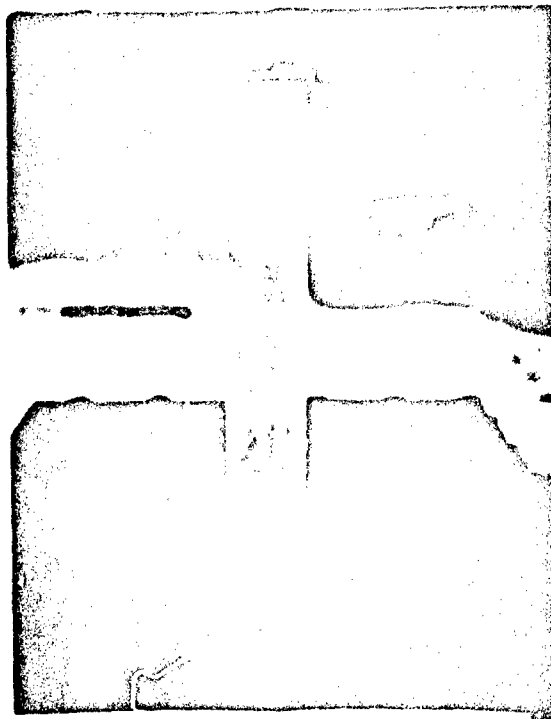


Figure 15

CYLINDRICAL SUBSTRATE
SHOWING FINE FIBROUS DEPOSIT

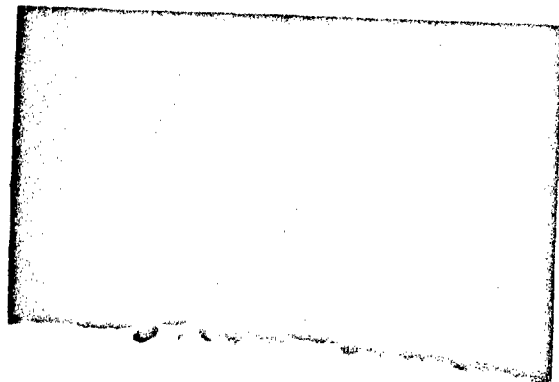


Figure 16
ERODED BeO DEPOSIT
MAGNIFICATION 130X

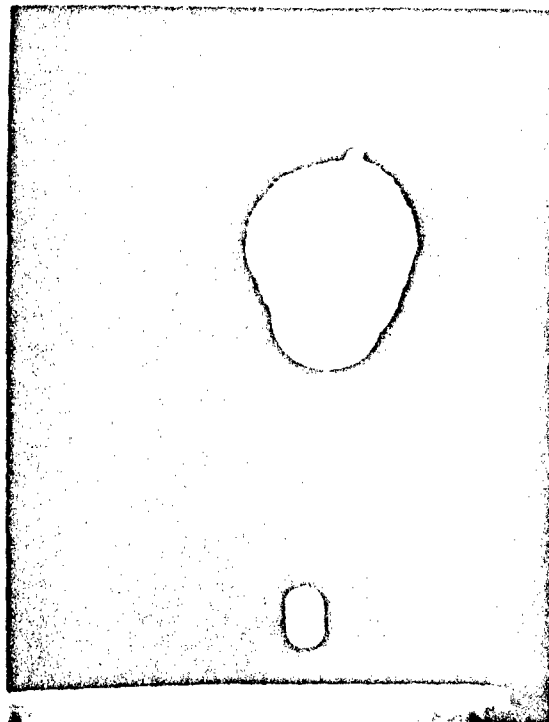


Figure 17

CRUCIBLE SUBSTRATE
SHOWING CRYSTAL GROWTH CONTINUOUS
WITH LIP OF CRUCIBLE

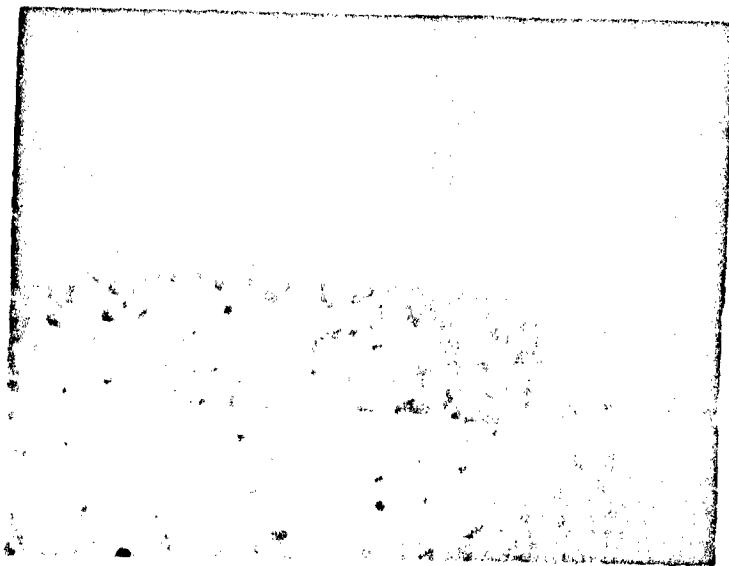


Figure 18

BeO DEPOSIT SHOWING FINE STRUCTURE
TEMPERATURE 1200°C
MAGNIFICATION 130X

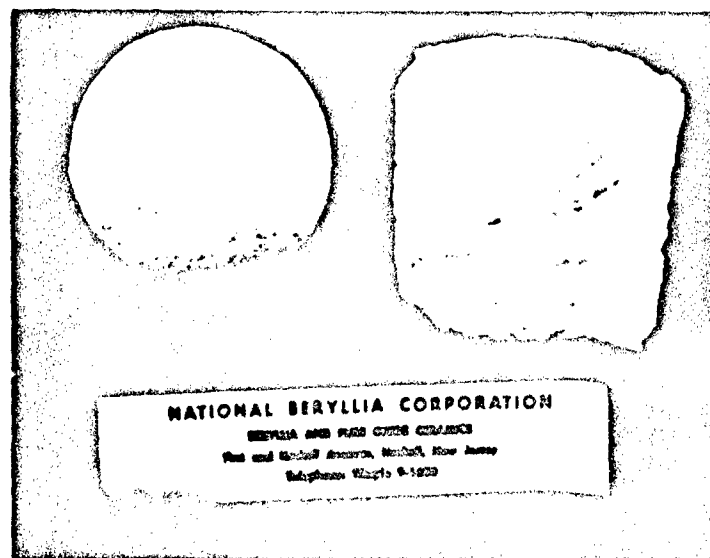


Figure 19

PURE BeO FOAM CERAMIC SPHERE
AND TYPICAL AS-CAST CYLINDRICAL BLANK

APPENDIX

TABULATION OF HYDRO-PYROLYTIC EXPERIMENTS

TABULATION OF HYDRO-PYROLYTIC EXPERIMENTS (Cont'd)

Run No.	Substrate Temp. °C	Flow Rate - l/min. HCl H ₂ CO ₂	GmBe Used	Time Min.	Purpose	Comments
21	1200	1 3 3	--	95	Study substrate geometry	Inverted crucible used
22	1200	1 3 3	--	--	Decrease wall temp.	Install heat reflectors
23	1400	1 3 3	--	20	Study effect of temp.	System clogged
24	1400	0.2 3 3	--	15	Study effect of Be conc.	" "
25	--	0.2 3 3	--	8	Redesign delivery system	Some clogging
26	1200	0.2 3 3	--	5	Correct clogging problem	Slight clogging
27	1100	0.2 3.5 3	1.2	26	" "	" "
28	1500	0.2 4 3	1.7	70	Study effect of Be conc.	No clogging
29	1400	0.4 4 3	5.8	150	" " "	Rough subs. surface
30	1400	0.4 4 3	--	150	Distribution of CO ₂	Slight deposit
31	1100	0.4 4 3	7.3	180	Study effect of temp.	Very slight deposit
32	1100	0.4 4 3	6.6	180	Prepare deposit	" " "
33	1200	0.4 4 3	9.4	240	Effect of temp.	" " "
34	1200	0.4 4 3	7.8	195	Prepare multiple deposit	" " "
35	1200	0.4 4 0.5	6.0	180	Study effect of CO ₂ conc.	" " "
36	1200	0.4 4 0.1	7.4	180	" " "	" " "
37	1200	0.4 4 0.1	6.8	180	Prepare multiple deposit	" " "
38	1300	0.4 4 0.1	2.8	75	Study effect of temp.	Pebble-like deposit
39	1200	0.4 3 0.1	--	60	Study flow of reactants	CO ₂ counter current to H ₂
40	1300	0.4 3 0.1	2.2	60	" " "	White deposit on subst.
41	1100	0.4 3 0.1	--	15	Study effect of temp.	Outer heater failed
42	1100	0.4 3 0.1	--	17	" " "	Inner heater failed
43	1200	0.4 3 0.1	2.8	60	" " "	Very slight deposit
44	1200	0.4 3 0.1	4.7	120	Prepare multiple deposit	" " "
45	1200	0.4 3 0.1	4.0	120	" " "	" " "

TABULATION OF HYDRO-PYROLYTIC EXPERIMENTS

Run No.	Substrate Temp. °C	Flow Rate - l/min.			GmBe Used	Time Min.	Purpose		Comments
		HCl	H ₂	CO ₂			Rig evaluation	Sl. pressure build-up	
1		2.5	1		1	7	" "	"	"
2		1	3		2.7	17	Inc. I.D. delivery tube	"	"
3		1	2		0.7	5	Heat delivery line	Clogging occurred	
4		1	2		4.3	30	Inc. line Temp.	Unrestricted flow	
5		1	2		9.4	60	Rig evaluation	"	"
6		1	2	1	--	--	"	"	"
7		1	2	1	--	--	"	"	"
8	950	1	2	1	1.8	15	Produce deposit	Substrate heater failed	"
9	1000	1	2	2	1.7	13	"	"	"
10	1000	1	2	2	8.6	60	"	Short columnar fibers formed	"
11	1000	1	3	3	12	80	"	Many columnar fibers formed	"
12	1000	1	3	3	9.5	60	Improve gas distribution	Many columnar fibers formed	"
13	1100	1	3	3	8.4	60	Study effect of temp.	Coating formed	"
14	1050	1	3	3	5.5	35	"	Light fiber growth	"
15	1150	1	3	3	5.1	38	"	"	"
16	1100	1	3	3	3.4	26	Produce deposit	Crystalline deposit formed	"
17	1200	1	3	3	--	37	Heater used as subst.	System clogged	"
18	1400	1	3	3	--	21	"	No coating on heater	"
19	1300	1	3	3	--	--	Prevent attack of heater	Coat wire with cement	"
20	1300	1	3	3	--	150	Prevent attack of heater	Recoat wire with cement	"

Run No.	Substrate Temp. °C	Flow Rate - l/min.			GmBe Used	Time Min.	Purpose	Comments
46	1250	0.4	3	0.1	--	75	Prepare multiple deposit	Very slight deposit
47	1200	0.4	3	0.15	4.1	90	Study flow of reactants	Slight deposit formed
48	1000	0.2	3	0.15	5.0	240	Study effect of conc. of reactants	Loose heavy deposit formed
49	1200	0.2	3	0.15	2.50	120	Study effect of temp.	Loose heavy deposit formed
50	1300	0.2	3	0.15	2.6	120	" " "	Loose heavy deposit formed
51	1300	0.1	3	0.15	1.3	180	Concentration of effects Effect of Be conc. Effect of temp & CO ₂ path	Rough loose deposit
52	1100	0.05	2	0.15	2.6	180		" "
53	1200	0.05	2	0.15	3.2	120		No deposit
54	1250	0.05	1	0.15	4.8	130	Effect of temp & CO ₂ path	" "
55	1300	0.05	2.5	0.15	1.9	120	Effect of Be-CO ₂ ratio	Sl. deposit formed
56	1450	0.03	2.5	0.15	1.0	135	" " " "	" "
57	1450	0.03	2.5	0.08	1.0	120	" " " "	" "
58	1450	0.03	2.5	0.04	0.9	120	Multiple deposit	" "
59	1400	0.1	2.0	0.15	9.3	480	Substrate geometry	Soft deposit formed
60	1350	0.1	2.0	0.15	1.9	120	Multiple deposit	" "
61	1350	0.1	2.0	0.15	2.0	120	" "	" "
62	1350	0.1	2.0	0.15	1.50	60	" "	" "
63	1350	0.1	2.0	0.15	1.1	30	Study effect of time	Substrate dislodged
64	1350	0.1	2.0	0.15	1.3	30	" " " "	Very slight deposit
65	1350	0.1	2.0	0.15	1.7	60	Multiple deposit	" "
66	1200	0.1	2.0	0.15	1.0	60	Substrate geometry	Rough loose deposit
67	1200	0.1	2.0	0.15	2.0	60	Multiple deposit	" "
68	1350	0.1	2.0	0.15	1.5	60	Study flow pattern	Slight deposit formed

TABULATION OF HYDRO-PYROLYTIC EXPERIMENTS (Cont'd)

Run No.	Substrate Temp. °C	Flow Rate - l/min.			Used	Min.	Purpose	Comments
		HCl	H ₂	CO ₂				
69	1350	0.1	2.0	0.05i 0.35f	1.4	60		Attempt to coat entire substrate
70	1350	0.1	2.0	0.35i 0.05f	1.3	60	Effect of progressive inc. in CO ₂ flow rate	Some deposit over entire substrate
71	1350	0.1	2.0	0.75i 0.05f	3.3	150	Effect of progressive dec. in CO ₂ flow rate Multiple deposit	Practically all of substrate coated
72	1100	0.1	2.0	0.75i 0.05f	0.0	24	Inc. substrate size	No deposit
73	1150	0.1	2.0	0.75i 0.05f	3.3	150	Inc. substrate size	Loose deposit
74	1150	0.1	2.0	0.75i 0.05f	3.4	150	Multiple deposit	Slight deposit
75	1150	0.1	2.0	1.5i 0.1f	0.9	35	"	"